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<b>(21) International Application Number:</b> PCT/SE99/01140 <b>(22) International Filing Date:</b> 23 June 1999 (23.06.99)  <b>(30) Priority Data:</b> 9802324-5                      30 June 1998 (30.06.98)                      SE  <b>(71) Applicant:</b> SANDVIK AB; (publ) [SE/SE]; S-811 81 Sandviken (SE).  <b>(72) Inventor:</b> CARPENTER, Michael, John; 166 Coleshill Road, Nuneaton (GB).  <b>(74) Agent:</b> TÅQUIST, Lennart; Sandvik AB, Patent Dept., S-811 81 Sandviken (SE).		<b>(81) Designated States:</b> MX, NO, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CEMENTED CARBIDE FOR OIL AND GAS APPLICATIONS  <b>(57) Abstract</b>  The present invention relates to a cemented carbide with excellent properties for oil and gas applications regarding resistance to the combined erosion and corrosion synergistic effects at temperatures between -50 and 300 °C, preferably 0-100 °C. The cemented carbide contains, in wt.%, 2.5-4.5 Co+Ni with a weight ratio Co/Ni of about 3, 0.25-0.6 Cr and 0.1 Mo wherein essentially all of the WC grains have a size < 1 µm and wherein the total carbon content is in the interval of 6.13 - (0.061±0.008) x binder phase (Co+Ni) content (wt.%).		

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## CEMENTED CARBIDE FOR OIL AND GAS APPLICATIONS

The present invention relates to a cemented carbide grade with special properties for oil and gas applications. Moreover the invention refers to the application of a corrosion-erosion resistant grade for choke valves to control the flow of multimedia fluid (gas, liquid and sand particles).

Cemented carbide for corrosion resistance demanding applications such as seal rings, bearings, bushings, hot rolls, etc. generally has a binder phase consisting of Co, Ni, Cr and Mo where the Cr and/or Mo act as corrosion inhibiting additions. An example of such a cemented carbide with a medium WC grain size is disclosed in EP 28 620. EP 568 584 discloses the use of a corrosion resistant cemented carbide with submicron WC grain size with excellent properties particularly for tools in the wood industry.

A critical component of subsea oil/gas production systems is the choke trim components, the primary function of which is to control the pressure and flow of well products. Under severe conditions of multi flow media, these components even when fitted with cemented carbide trims may suffer from extreme mass loss by exposure to solid particle erosion, acidic corrosion, erosion-corrosion synergy and cavitation mechanisms.

The opportunity to maintain or replace such equipment in the field especially in offshore deep water sites is limited by weather conditions. It is therefore essential that reliable and predictable products form part of the subsea system.

The composition of the cemented carbide grades presently used for withstanding conditions of service in this environment generally consist of tungsten carbide (WC) as the hard component and cobalt (Co) or nickel

(Ni) as the binder material to cement together the WC crystals.

To meet the demands of hardness and toughness, the amount of binder and/or the WC grain size are varied and cobalt is generally accepted as the optimum binder constituent. Where corrosion is the predominant factor then the binder material is usually of nickel or nickel+chromium (Ni+Cr) composition.

Analogous to stainless steels Cr and Ni alloys have improved passivity by reducing the critical currents involved in corrosion, however (Cr+Ni) are not so resistant to halides (seawater) or inorganic acids. For these conditions the addition of molybdenum gives improved corrosion resistance in addition to improving binder strength of Ni.

Recent experimental work including field trial evaluation has proven that in cases of high erosion conditions under a corrosion media then the mechanism of mass loss is a combination of each condition but moreover synergistic.

The present invention relates to the use of cemented carbide with excellent properties regarding resistance to the combined erosion and corrosion synergistic effects at temperatures between -50 and 300°C, preferably 0-100°C.

Resistance to particle erosion under corrosion environment has been achieved by using a specifically optimised multi alloy binder sintered with a submicron grain size WC i.e. essentially all of the WC grains have a size <1 µm. The cemented carbide according to the invention has the composition, in wt%, 2.5-4.5 Co+Ni with a weight ratio Co/Ni of about 3, 0.25-0.6 Cr and about 0.1 Mo.

In one preferred embodiment the cemented carbide has the composition 3.3 % Co, 1.1 % Ni, 0.52 % Cr, 0.1 %

Mo with the balance of WC with an average grain size of 0.8  $\mu\text{m}$ .

In another preferred embodiment the composition is 1.9 % Co, 0.7 % Ni, 0.3% Cr, 0.1 % Mo with the balance of WC of 0.8  $\mu\text{m}$ .

The carbon content within the sintered cemented carbide must be kept within a narrow band in order to retain a high resistance to corrosion and wear as well as toughness. The total carbon content shall be in the interval of  $6.13 - (0.061 \pm 0.008) \times \text{binder phase (Co+Ni)}$  content (wt-%), preferably  $6.13 - (0.061 \pm 0.005)$ .

The hardness of the cemented carbide according to the invention shall be  $>1875$ , preferably  $>1900$  HV30 and the TRS as determined according to ISO 3327 type B test pieces shall be  $>2100$ , preferably  $>2200$  N/mm<sup>2</sup>.

The cemented carbide used in this invention is manufactured by conventional powder metallurgical methods milling, pressing shaping and sinterhipping.

The cemented carbide according to the invention is particularly applicable for the choke trim components used in oil and gas industry where components are subjected to high pressures of multi media fluid where there is a corrosion environment including seawater.

#### 25 Example 1

A cemented carbide according to the invention had the composition 3.3 % Co, 1.1 % Ni, 0.6 % Cr<sub>3</sub>C<sub>2</sub>, 0.1 % Mo with the balance of WC, a hardness of 1900 HV30 and transverse rupture strength (TRS) of 2350 N/mm<sup>2</sup> with a mean WC grain size of 0.6  $\mu\text{m}$ . It was tested against commercially available cemented carbide grades one made from 6 % Co and the other from 6 % Ni both with the balance of WC (0.8  $\mu\text{m}$ ) under the following simulated test conditions:

- synthetic seawater
- sand 18 m/s
- CO<sub>2</sub> 1 Bar
- temperature 54°C.

5 The following results were obtained. Units material loss: mm/year

Grade	corrosion	erosion	synergistic	total
WC 6%Co	0.02	0.09	0.35	0.46
WC 6%Ni	0.015	0.265	0.17	0.45
10 invention	0.015	0.06	0.025	0.10

### Example 2

Cemented carbides were made according to the invention with the composition 3.3 % Co, 1.1 % Ni, 0.6 % Cr<sub>3</sub>C<sub>2</sub>, 0.1 % Mo with the balance of WC 0.8 μm, referred to as grade 1 and grade 2 consisting of a similar alloy composition but with reduced proportions of 1.9 % Co, 0.7 % Ni, 0.35 % Cr<sub>3</sub>C<sub>2</sub>, 0.1 % Mo with the balance of WC. These materials had hardness values of 1900HV30 and 1910HV30 and transverse rupture strength (TRS) of 2350 N/mm<sup>2</sup> and 2350 N/mm<sup>2</sup> respectively each with a mean WC grain size of 0.6 μm. They were tested against commercially available cemented carbide grades under the following simulated test conditions of seawater and sand.

Flow rate : 90 m/sec and impingement angles of 30° and 90°.

The following results were obtained. Units material loss: mm<sup>3</sup>/kg sand

Grade	erosion 30°	erosion 90°
WC 6%Co	1.6	1.4
WC 6%Ni	2.1	1.6
1 (invention)	0.5	0.3
35 2 (invention)	0.25	0.15

Example 3

A cemented carbide according to the invention with the composition 3.3 % Co, 1.1 % Ni, 0.6 % Cr<sub>3</sub>C<sub>2</sub>, 0.1 % Mo, with the balance of WC and a hardness of 1900HV30 and transverse rupture strength (TRS) of 2350 N/mm<sup>2</sup> with a mean WC grain size of 0.6 µm was tested against commercially available cemented carbide grades. Test conditions of air and sand at 200 m/s:

Flow rate: 200 m/s air and impingement angles of 30° and 90°.

The following results were obtained. Units material loss: mm<sup>3</sup>/kg sand.

Grade	erosion	
	30°	90°
WC 6%Co	2.5	4.0
WC 6%Ni	2.6	5.6
Invention	0.8	1.4

The cemented carbide according to the invention shows significant reduction in wear as measured by volume loss.

Claims

1. Cemented carbide with excellent properties for oil and gas applications regarding resistance to the combined erosion and corrosion synergistic effects at  
5 temperatures between -50 and 300°C, preferably 0-100°C  
c h a r a c t e r i s e d in containing, in wt%, 2.5-4.5  
Co+Ni with a weight ratio Co/Ni of about 3, 0.25-0.6 Cr  
and 0.1 Mo wherein essentially all of the WC grains have  
a size  $<1\text{ }\mu\text{m}$  and wherein the total carbon content is in  
10 the interval of  $6.13-(0.061\pm 0.008) \times \text{binder phase}$   
(Co+Ni) content (wt-%).
2. Cemented carbide according to the previous claim  
c h a r a c t e r i s e d in the composition 3.3 % Co,  
1.1 % Ni, 0.52 % Cr, 0.1 % Mo with balance of WC.
- 15 3. Cemented carbide according to claim 1  
c h a r a c t e r i s e d in the composition 1.9 % Co,  
0.7 % Ni, 0.3% Cr, 0.1 % Mo with balance of WC.
4. Cemented carbide according to any of the  
previous claims c h a r a c t e r i s e d in a carbon  
20 content in the interval of  $6.13-(0.061\pm 0.005) \times \text{binder}$   
phase (Co+Ni) content (wt-%).
5. Use of a cemented carbide according to claims 1-  
4 for oil and gas applications particularly for  
components, the primary function of which is to control  
25 the pressure and flow of well products.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01140

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C22C 29/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 8002569 A1 (SANDVIK AKTIEBOLAG), 27 November 1980 (27.11.80)  --	1-5
A	WO 9213112 A1 (SANDVIK AB), 6 August 1992 (06.08.92)  -- -----	1-5

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8002569 A1	27/11/80	AT 9169 E,T DK 156226 B,C DK 215280 A EP 0028620 A,B JP 1027143 B JP 56500748 T SE 420844 B,C SE 7904331 A US 4497660 A	15/09/84 10/07/89 18/11/80 20/05/81 26/05/89 04/06/81 02/11/81 18/11/80 05/02/85
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